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## Transparent Barrier Urethanes Based on Polyethylene Soft Segments

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## Abstract

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A series of polyurethane elastomers has been synthesized through copolymerization of polyethylene soft segments and methylene bis(4-phenylisocyanate) (MDI) and hydrogenated MDI (H<sub>12</sub>MDI). Polyethylene soft segments were prepared by the hydrogenation of polybutadiene polyols, either before or after copolymer synthesis. Polyols from three different suppliers were used as precursors and ranged in branch content from 15% to ~90%. Flexible, transparent materials were produced. The mechanical and barrier properties of these urethanes were evaluated for comparison with the performance of traditional flexible barrier materials (e.g., butyl rubber). Solvent uptake and swelling measurements were used to evaluate barrier performance. Branch content in the soft segment was found to affect both mechanical properties and solvent resistance, with low branch content leading to superior performance. Solvent diffusion coefficients for the materials were in the 10<sup>-8</sup>-cm<sup>2</sup>/s range, comparable to those exhibited by flexible high barrier materials.

## ACKNOWLEDGMENTS

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# TRANSPARENT BARRIER URETHANES BASED ON POLYETHYLENE SOFT SEGMENTS

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## 1. Introduction

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Segmented polyurethane elastomers based on olefinic soft segments are of interest for use in a variety of applications. The inertness of the olefinic segment, coupled with the strong microphase segregation in these systems, lends these materials many desirable characteristics, such as solvent resistance, good electrical properties, low moisture permeability, and biocompatibility.[1-4] When the soft segments are fully saturated, the chemical inertness is improved even further, and the materials gain resistance to hydrolysis and oxidation.[2] This chemical inertness, coupled with the materials' inherent processability, makes these olefinic urethanes attractive for use in barrier applications, including protective clothing, masks and gloves.

A plethora of publications about the synthesis and evaluation of polyurethanes that are based on saturated olefinic soft segments appeared between the late 1970s and the early 1990s and focused largely on polyisobutylene and hydrogenated polybutadiene soft segment chemistries.[2, 5-12] More emphasis was placed on the latter, because of the commercial availability of butadiene polyols and problematic synthesis leading to inferior performance of the isobutylene-based systems.[10] The physical properties of the hydrogenated polybutadiene (PBD) urethanes, including mechanical performance, thermal transition temperatures, degree of phase separation, and transparency have been found to depend on a number of factors, including degree of hydrogenation [5], soft segment molecular weight [13], and synthesis conditions.[9] A comparison of different studies of polyurethanes having fully saturated soft segments of roughly equal molecular weight also suggests that the use of soft segments supplied by different manufacturers, with the associated differences in branching content and functionality, may alter the properties of the urethanes significantly.

In this study, we investigated a novel series of polyurethanes based on hydrogenated, hydroxy-terminated polybutadiene (PBD) soft segments and two different hard segments. These soft segments are unique in that they are produced by a cost-effective process, have functionality of nearly exactly 2.0, and have very low branch content in comparison to commercially available PBD polyols. Our aim was to produce melt-processable polyurethanes with elastomeric mechanical properties, transparency, and good resistance to the sorption and diffusion of solvents. We have prepared and evaluated the mechanical and solvent sorption properties of a series of polyurethane elastomers that are based on these novel soft segments, as well as a series of polyurethane elastomers produced with commercial soft segments of similar

chemistry. Properties are found to depend on hard segment content, hard segment chemistry, properties of the polyol, and the order of the hydrogenation and polymerization reactions.

## 2. Experimental Procedures

### 2.1 Materials

Polyurethanes were synthesized from two commercial diisocyanates, methylene bis(4-phenylisocyanate) (MDI) and hydrogenated MDI ( $H_{12}$ MDI), 1,4-butanediol (BD) chain extender, and hydroxy-terminated polybutadiene (HTPBD) or hydrogenated hydroxy-terminated polybutadiene (HTPE) soft segments. Chemical structures of the precursors are illustrated in Figure 1.

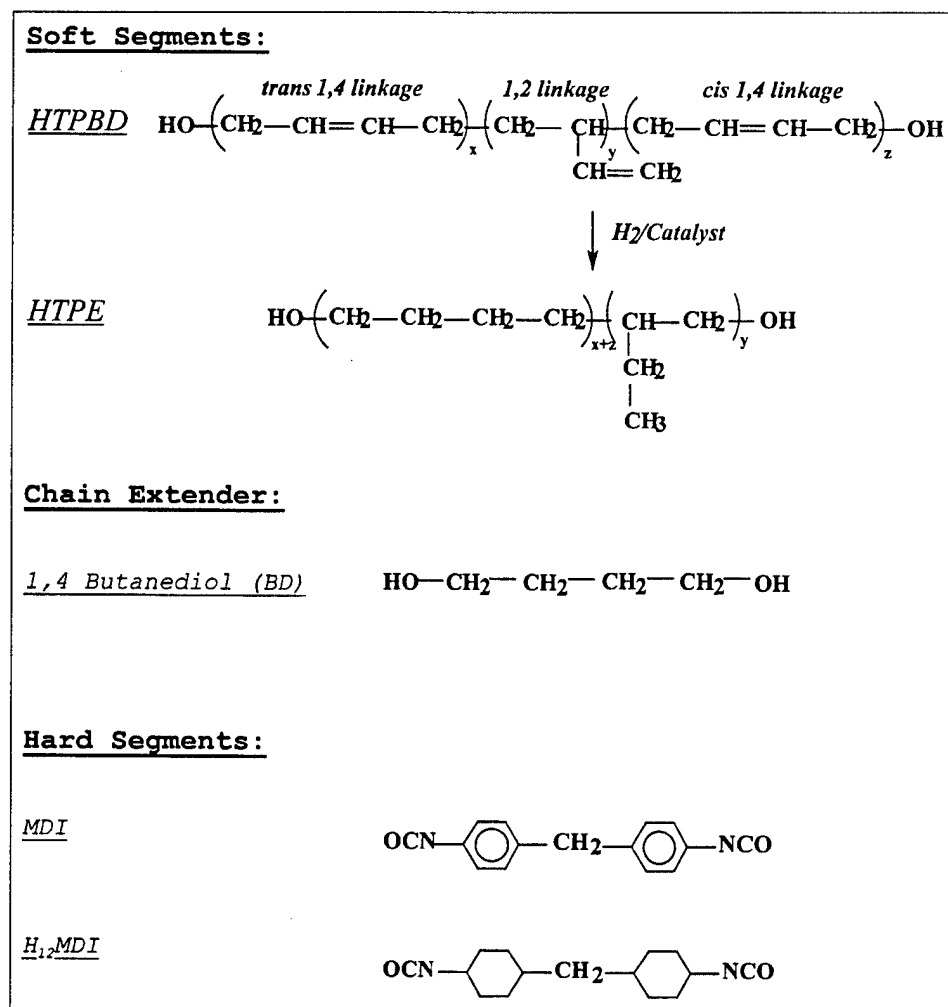


Figure 1. Chemical Structures of Starting Materials.



HTPBD and HTPE polyol soft segments were prepared by the research group of the late Professor F. Tudos, Macromolecular Chemistry, Hungarian Academy of Sciences in Budapest, Hungary. The polyols were prepared by the free radical "isodisperse telechelic polymerization" method under non-isothermal conditions. This method, which was pioneered by the Tudos group, provides a cost-effective route to the preparation of telechelic polymers with low polydispersity and functionality of  $F = 2.0 \pm 0.05$ .<sup>[15]</sup> Molecular weights and polydispersities were determined by gel permeation chromatography. Functionality was determined by ultraviolet (UV) spectroscopy. Branch contents (percent 1,2 linkages) were determined using proton nuclear magnetic resonance (NMR) spectroscopy and Fourier transform infrared (FTIR) spectroscopy. Some samples were hydrogenated before polymerization (HTPE 2136) via a Parr hydrogenation apparatus and a hydrogenated palladium/carbon (Pd/C) catalyst.<sup>[16]</sup>

HTPBD and pre-hydrogenated HTPBD (HTPE) soft segments were also obtained from Japan Synthetic Rubber (JSR) and Nippon Soda (NS), respectively. The molecular weight, polydispersity, functionality, and branch content for these materials have been previously measured by other groups.<sup>[8,9]</sup> Data from the literature are included in Table 1.

Table 1. Soft Segment Properties

Soft Segment Source	Initial State	$M_n$ (g/mole)	PDI <sup>a</sup>	$F_n$	1,2 Content (percent)
Tudos	HTPBD	1245	1.34	1.62	15
	HTPBD	1552	1.34	2.10	15
	HTPBD	1870	1.62	1.90	17
	HTPBD	5230	1.72	1.98	17
	HTPE	2136	1.79	2.01	17
Japan Synthetic Rubber	HTPBD	2000 <sup>b</sup>	--	1.98 [14]	43
Nippon Soda	HTPE	1000 <sup>b</sup>	--	--	--
	HTPE	2000 <sup>b</sup> /2100 [8,9]	1.5 [8]	1.8 [8,9]	82 [9]
	HTPE	3000 <sup>b</sup>	--	--	--

<sup>a</sup>PDI = polydispersity index

<sup>b</sup>Reported by the manufacturer.

## 2.2 Polyurethane Synthesis

Segmented polyurethane block copolymers were synthesized via standard urethane chemistry in 4:1 toluene-dimethyl formamide (DMF) mixtures. The hydroxy-terminated hydrophobic oligomers were dried through toluene-water

azeotrope distillation under dry argon and then end capped with MDI. The chain extender (BD) was added drop-wise in the second stage of the synthesis, which was allowed to continue overnight to achieve high molecular weight. Finally, the polymer was either precipitated in excess methanol or directly cast into thin films from reaction solution.

Polyurethane block copolymers were prepared from all soft segments listed in Table 1. Polyurethanes were prepared from soft segments provided by each of the three sources with hard segment contents ranging from 14% to 40% and with both MDI and H<sub>12</sub>MDI as the hard segments. The stoichiometry of the copolymers prepared is summarized in Table 2.

Table 2. Polyurethane Formulations

Soft Segment (SS)	SS Source	SS M <sub>n</sub> (g/mole)	Hard Segment (HS)	SS/HS/BD	percent HS
h-HTPBD	Tudos	1552	MDI	1/1/0	14
h-HTPBD	Tudos	1552	H <sub>12</sub> MDI	1/1/0	14
h-HTPBD	Tudos	1245	MDI	1/4/3	40
h-HTPBD	Tudos	1870	MDI	1/3/2	27
h-HTPBD	Tudos	1870	MDI	1/6/5	39
h-HTPBD	Tudos	5260	MDI	1/5/4	18
HTPE	Tudos	2136	MDI	1/3/2	24
HTPE	Tudos	2136	H <sub>12</sub> MDI	1/3/2	25
h-HTPBD	JSR	1970	MDI	1/3/2	26
h-HTPBD	JSR	1970	MDI	1/6/5	38
h-HTPBD	JSR	1970	H <sub>12</sub> MDI	1/6/5	39
HTPE	NS	1000	MDI	1/1/0	19
HTPE	NS	1000	MDI	1/3/2	39
HTPE	NS	1000	H <sub>12</sub> MDI	1/3/2	40
HTPE	NS	2000	MDI	1/2/1	20
HTPE	NS	2000	MDI	1/3/2	26
HTPE	NS	2000	H <sub>12</sub> MDI	1/3/2	27
HTPE	NS	2000	MDI	1/6/5	38
HTPE	NS	3000	MDI	1/3/2	19

### 2.3 Hydrogenation

For those polyurethane block copolymers synthesized via HTPBD soft segments, post-synthesis hydrogenation was performed to saturate the soft segments. (These materials are designated as having h-HTPBD soft segments, to distinguish

them from materials having pre-hydrogenated soft segments designated HTPE.) The hydrogenation was performed chemically by *p*-toluenesulfonhydrazide. Polyurethanes were dissolved into mixed solvent (toluene-DMF, 4:1) and refluxed at 110° C for about 30 minutes. A 500% excess of *p*-toluenesulfonhydrazide was then added. The reaction was stopped when the color of solution became darker. The reaction was confirmed by FTIR, which showed nearly complete hydrogenation indicated by the disappearance of peaks at 965.7, 911.7, 722.7 cm<sup>-1</sup> corresponding to the 1,4-trans, 1,2-, and 1,4-cis double bond absorptions. We have elected to hydrogenate HTPBD after incorporating it in the polyurethane since hydrogenation of the HTPBD prepolymer may cause changes in the functionality. Hydrogenation causes no visible change in the amide double bond (~ 1500 cm<sup>-1</sup>), which indicates that the urethane linkage is not degraded during the hydrogenation reaction. This selective post-hydrogenation provides a new route to the synthesis of saturated polyurethanes.

## 2.4 Sample Preparation

Polyurethane films of 0.5- to 1.0-mm thickness were cast from solutions at elevated temperature followed by vacuum drying for two days and extraction with hexane for three days to remove any unreacted small molecules.

## 2.5 Mechanical Characterization

Uniaxial stress-strain experiments were performed on a table model Instron Series 9 tensile testing machine. Specimens for mechanical testing were prepared with an American Society for Testing Materials (ASTM) D1708 standard die. Sample dimensions were 4.75 mm wide and 22.3 mm in gauge length. The experiments were performed at room temperature at 12.5-mm/min constant strain rate.

## 2.6 Barrier Property Evaluation

Barrier properties were quantified via immersion studies. Total solvent uptake was recorded, and diffusion coefficients were estimated by analyzing the weight versus time curves. The procedure for immersion experiments was as follows. Pre-weighed samples, approximately 2 cm in diameter and 1 to 2 mm thick, were immersed in excess solvent at room temperature, removed at various time intervals, blotted with two sets of filter paper, and immediately weighed. Weight gain is recorded and the samples are then returned to the immersion vessel; the procedure is repeated until the samples reach constant weight (typically 4 to 8 days). Polymers were evaluated for sorption of acrylonitrile, toluene and 1,5-dichloropentane. Diffusion constants are extracted from the sorption data as described next.

## 2.7 Diffusion Coefficients

Diffusion behavior, as quantified by Fick's law, may be represented by the following equation [17]

$$dC/dt = d/dx (D(dC/dx)) \quad (1)$$

in which  $D$  is the diffusion coefficient,  $C$  is the concentration of diffusing species,  $x$  is the direction of flow, and  $t$  is time. Solutions to this equation for various geometries and boundary conditions are available.

One solution for diffusion at short times that can be used for immersion uptake studies is [18,19]

$$M_t/M_\infty = 4/d [Dt / \pi]^{1/2} \quad (2)$$

in which  $M_t$  is the mass uptake at time  $t$ ,  $M_\infty$  is the mass uptake at equilibrium, and  $d$  is the thickness of sample. From a graph of  $M_t/M_\infty$  versus  $t^{1/2}$ , one can calculate the diffusion coefficient as [17]

$$D = \pi S^2 d^2 / 4 \quad (3)$$

in which  $S$  is defined as the slope. If  $t_s$  is defined as the point where  $M_t/M_\infty = 0.5$ , Equation (3) can be simplified to [17]

$$D = (0.0492 / t_s) d^2 \quad (4)$$

The approximation given by Equation (4) yields an estimate of the diffusion coefficient to within 0.001% of that calculated using Equation (3). [17] Equation (4) was used to extract diffusion coefficients from sorption measurements in this study.

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## 3. Results

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### 3.1 General

All segmented polyurethane copolymers prepared were transparent and elastomeric in the as-cast state, as desired. Transparency is not uncommon for hydrophobic soft segment, polyurethane elastomers containing 40% hard segment or less, which have been prepared by solution polymerization.[2,9] However, certain types of hard segments and/or bulk synthesis techniques may induce translucency or opacity in olefinic urethanes.[2,9]

The mechanical properties of the polymers prepared in this study are compiled in Table 3. The moduli of the copolymers range from 4 to 50 MPa for materials with hard segment contents of 30% or less and from 100 to 500 MPa for copolymers with hard segment content of ~40%. Ultimate elongations and strengths are in the range of 50% to 600% and 5 to 20 MPa, respectively. These properties are generally comparable to those that have been reported for other polyurethane copolymers with olefinic soft segments.[2,5,9,11] However, higher ultimate elongations are achieved for the materials prepared in this study relative to those reported by other groups for materials of similar chemistry and preparation.[9] The materials synthesized with the novel soft segment precursors provided by the Tudos group show a superior combination of high stiffness and high elongation relative to other materials prepared in this study and by others.[5,9,11]

The barrier properties of these segmented, olefinic polyurethanes are also quite impressive. These elastomers were insoluble in all pure solvents tested, including aprotic solvents such as DMF and tetrahydrofuran (THF). The results of solvent immersion experiments are compiled in Tables 4 and 5. The immersion experiments showed low uptake of a small, polar solvent molecule ( $\text{CH}_3\text{CN}$  = acrylonitrile) by the HTPE and h-HTPBD urethanes and moderate uptake of a chlorinated, aliphatic solvent. The lowest sorption numbers reported for 1,5-dichloropentane, in the range of 20% to 35%, are similar to those reported previously for cross-linked urethane systems with similar hard segment content.[2] While many of the materials swelled considerably when immersed in toluene, some high hard segment formulations were fairly resistant to this solvent, sorbing only moderate amounts (~35% to 50%) upon extended immersion.

The solvent diffusion coefficients measured for these urethane elastomers are also very impressive. For acrylonitrile and dichloropentane, diffusion coefficients are on the order of  $10^{-8}$  to  $10^{-9}$   $\text{cm}^2/\text{s}$ . These numbers rival those reported for elastomers and rubbers known to have the highest performance in barrier applications.[16]

### **3.2 Important Performance Parameters**

In general, the mechanical and barrier performance of the olefinic, segmented copolymers studied was found to depend strongly on three parameters in their formulation: 1) hard segment chemistry, 2) hard segment content, and 3) soft-segment characteristics. The effects of each parameter are highlighted individually in the following paragraphs.

#### **3.2.1 Effects of Hard Segment Chemistry**

Two types of hard segment were used in the preparation of urethanes: methylene bis(4-phenylisocyanate), or MDI, and hydrogenated methylene bis(4-

Table 3. Mechanical Properties, Compiled

Soft Segment (SS)	SS Source	SS $M_n$ (g/mole)	Hard Segment (HS)	SS/HS/BD	Percent HS	Modulus (MPa)	UTS <sup>a</sup> (MPa)	Elongation (percent)
h-HTPBD	Tudos	1552	MDI	1/1/0	14	40.8	3.2	230
h-HTPBD	Tudos	1552	H <sub>12</sub> MDI	1/1/0	14	2.4	0.4	350
h-HTPBD	Tudos	1245	MDI	1/4/3	40	486.2	32.8	150
h-HTPBD	Tudos	1870	MDI	1/3/2	27	50.3	6	57
h-HTPBD	Tudos	1870	MDI	1/6/5	39	279.3	24.6	105
h-HTPBD	Tudos	5260	MDI	1/5/4	18	5.8	7.9	431
HTPE	Tudos	2136	MDI	1/3/2	24	22.6	20.7	430
HTPE	Tudos	2136	H <sub>12</sub> MDI	1/3/2	25	11.2	18.1	483
h-HTPBD	JSR	1970	MDI	1/3/2	26	12.5	8.9	227
h-HTPBD	JSR	1970	MDI	1/6/5	38	103.5	11.4	85
h-HTPBD	JSR	1970	H <sub>12</sub> MDI	1/6/5	39	162	15	130
HTPE	NS	1000	MDI	1/1/0	19	1.6	4.7	43.5
HTPE	NS	1000	MDI	1/3/2	39	46.8	20.8	285
HTPE	NS	1000	H <sub>12</sub> MDI	1/3/2	40	74.7	20.9	340
HTPE	NS	2000	MDI	1/2/1	20	3.8	8.9	561
HTPE	NS	2000	MDI	1/3/2	26	11.5	16	370
HTPE	NS	2000	H <sub>12</sub> MDI	1/3/2	27	5.6	11.9	490
HTPE	NS	2000	MDI	1/6/5	38	42.1	26.4	270
HTPE	NS	3000	MDI	1/3/2	19	3.2	8.4	400

<sup>a</sup>UTS = ultimate tensile strength

Table 4. Barrier Properties: Part A. Solvent Uptake, Compiled

Soft Segment (SS)	SS Source	SS $M_n$ (g/mole)	Hard Segment (HS)	percent HS	CH <sub>3</sub> CN* (percent)	DCP (percent)	Toluene (percent)
h-HTPBD	Tudos	1245	MDI	40	6.41	34.50	35.20
h-HTPBD	Tudos	1870	MDI	27	4.58	46.7	111.6
h-HTPBD	Tudos	1870	MDI	39	--	23.5	--
h-HTPBD	Tudos	5260	MDI	18	3.11	87.9	210
HTPE	Tudos	2136	MDI	24	2.45	35.8	89.7
HTPE	Tudos	2136	H <sub>12</sub> MDI	25	3.3	47.7	290.4
h-HTPBD	JSR	1970	MDI	26	41.03	--	196
h-HTPBD	JSR	1970	MDI	38	--	23.2	--
h-HTPBD	JSR	1970	H <sub>12</sub> MDI	39	--	--	--
HTPE	NS	1000	MDI	19	4.47	--	273.2
HTPE	NS	1000	MDI	39	4.22	33.3	52.4
HTPE	NS	1000	H <sub>12</sub> MDI	40	--	75.5	--
HTPE	NS	2000	MDI	20	2.71	--	216.2
HTPE	NS	2000	MDI	26	37.1	48.9	--
HTPE	NS	2000	H <sub>12</sub> MDI	27	15.8	77.7	511.3
HTPE	NS	2000	MDI	38	9.52	32.5	50.28

\*Acrylonitrile.

Table 5. Barrier Properties: Part B. Diffusion Coefficients, Compiled

Soft Segment (SS)	SS Source	SS $M_n$ (g/mole)	Hard Segment (HS)	percent HS	CH <sub>3</sub> CN (cm <sup>2</sup> /s)	DCP (cm <sup>2</sup> /s)	Toluene (cm <sup>2</sup> /s)
h-HTPBD	Tudos	1245	MDI	40	1.49E-08	--	5.11E-08
h-HTPBD	Tudos	1870	MDI	27	4.41E-08	--	3.63E-08
h-HTPBD	Tudos	1870	MDI	39	--	--	--
h-HTPBD	Tudos	5260	MDI	18	8.46E-08	--	5.14E-08
HTPE	Tudos	2136	MDI	24	5.30E-08	--	3.00E-07
HTPE	Tudos	2136	H <sub>12</sub> MDI	25	1.80E-08	6.13E-08	4.10E-07
h-HTPBD	JSR	1970	MDI	26	--	--	--
h-HTPBD	JSR	1970	MDI	38	--	--	--
h-HTPBD	JSR	1970	H <sub>12</sub> MDI	39	--	--	--
HTPE	NS	1000	MDI	19	1.49E-08	--	2.01E-07
HTPE	NS	1000	MDI	39	3.01E-08	2.98E-08	3.20E-07
HTPE	NS	1000	H <sub>12</sub> MDI	40	--	--	--
HTPE	NS	2000	MDI	20	1.32E-08	--	1.41E-07
HTPE	NS	2000	MDI	26	3.13E-09	--	--
HTPE	NS	2000	H <sub>12</sub> MDI	27	2.98E-09	--	2.53E-07
HTPE	NS	2000	MDI	38	--	--	--



phenylisocyanate), or H<sub>12</sub>MDI. Both are common diisocyanates used in the preparation of polyurethanes. The effect of hydrogenation of the hard segment on urethane properties is highlighted in the examples shown in Table 6. For polyurethane copolymers with hard segment content of ~30% or less, the hydrogenation of the diisocyanate results in increased elastomeric character of the polymer, i.e., decreased strength and modulus and increased ultimate elongation. At higher hard segment contents, ~40%, the mechanical properties of the H<sub>12</sub>MDI urethanes, including modulus, strength, and elongation, are superior to those of the MDI urethanes.

The barrier properties of h-HTPBD and HTPE urethanes are generally degraded by the hydrogenation of the hard segment. Polymers prepared with H<sub>12</sub>MDI have increased total solvent uptake relative to those prepared with MDI, particularly for the chlorinated and aromatic solvent (see Tables 7 and 8).

### 3.2.2 Effects of Hard Segment Content

Polyurethanes based on olefinic soft segments from each manufacturer were prepared with hard segment contents varying from ~15% to 40%. Property changes with hard segment content are typical of what one would expect for urethane elastomers (see Figures 2 and 3, Tables 9 through 11). Mechanical property evaluations showed that increased hard segment contents led to increased modulus and strength and decreased ultimate elongations.

Barrier property evaluation showed that increasing hard segment contents resulted in decreased solvent uptake for toluene and dichloropentane. The trends in acrylonitrile uptake with hard segment content are less well behaved, but there is some indication that acrylonitrile uptake is slightly higher at hard segment content of ~40% than at hard segment content of ~15% to 20% and that intermediate hard segment contents have the poorest performance for urethanes based on soft segments supplied by Nippon Soda and Japan Synthetic Rubber.

### 3.2.3 Effects of Soft Segment Type

The properties of the segmented, polyurethane, block copolymers studied are significantly different for materials prepared with soft segments from different suppliers (see Tables 12 through 14 and Figures 4 and 5). For a given hard segment content and type, the materials prepared from the Tudos precursors have the highest modulus. For urethanes with hard segment content of less than ~38%, ultimate strengths and elongations are similar for materials made with the Tudos and Nippon Soda precursors and higher than those achieved for materials prepared from Japan Synthetic Rubber precursors.

Barrier properties of the urethane elastomers were also affected by soft segment type. The lowest uptake for all solvents studied was attributed to the polymers prepared with the Tudos precursors. The resistance of the Tudos urethanes to

Table 6. Mechanical Properties as a Function of Hard Segment Type

Soft Segment (SS)	SS Source	SS $M_n$ (g/mole)	SS/HS/BD	percent HS	Hard Segment (HS)	Modulus (MPa)	UTS (MPa)	Elongation (percent)
h-HTPBD	Tudos	1552	1/1/0	14	MDI	40.8	3.2	230
h-HTPBD	Tudos	1552	1/1/0	14	H <sub>12</sub> MDI	2.4	0.4	350
HTPE	Tudos	2136	1/3/2	24	MDI	22.6	20.7	430
HTPE	Tudos	2136	1/3/2	25	H <sub>12</sub> MDI	11.2	18.1	483
HTPE	NS	2000	1/3/2	26	MDI	11.5	16	370
HTPE	NS	2000	1/3/2	27	H12MDI	5.6	11.9	490
HTPE	NS	1000	1/3/2	39	MDI	46.8	20.8	285
HTPE	NS	1000	1/3/2	40	H <sub>12</sub> MDI	74.7	20.9	340
h-HTPBD	JSR	1970	1/6/5	38	MDI	103.5	11.4	85
h-HTPBD	JSR	1970	1/6/5	39	H <sub>12</sub> MDI	162	15	130

Table 7. Barrier Properties: Part A. Solvent Uptake as a Function of Hard Segment Type

Soft Segment (SS)	SS Source	SS $M_n$ (g/mole)	SS/HS/BD	percent HS	Hard Segment (HS)	CH <sub>3</sub> CN (percent)	DCP (percent)	Toluene (percent)
HTPE	Tudos	2136	1/3/2	24	MDI	2.45	35.8	89.7
HTPE	Tudos	2136	1/3/2	25	H <sub>12</sub> MDI	3.3	47.7	290.4
HTPE	NS	2000	1/3/2	26	MDI	37.1	48.9	--
HTPE	NS	2000	1/3/2	27	H <sub>12</sub> MDI	15.8	77.7	511.3
HTPE	NS	1000	1/3/2	39	MDI	4.22	33.3	52.4
HTPE	NS	1000	1/3/2	40	H <sub>12</sub> MDI	--	75.5	--

Table 8. Barrier Properties: Part B. Diffusion Coefficients as a Function of Hard Segment Type

Soft Segment (SS)	SS Source	SS $M_n$ (g/mole)	SS/HS/BD	percent HS	Hard Segment (HS)	CH <sub>3</sub> CN* (cm <sup>2</sup> /s)	DCP (cm <sup>2</sup> /s)	Toluene (cm <sup>2</sup> /s)
HTPE	Tudos	2136	1/3/2	24	MDI	5.30E-08	--	3.00E-07
HTPE	Tudos	2136	1/3/2	25	H <sub>12</sub> MDI	1.80E-08	6.13E-08	4.10E-07
HTPE	NS	2000	1/3/2	26	MDI	3.13E-09	--	--
HTPE	NS	2000	1/3/2	27	H <sub>12</sub> MDI	2.98E-09	--	2.53E-07

Table 9. Mechanical Properties as a Function of Hard Segment Content

Soft Segment (SS)	SS Source	SS $M_n$ (g/mole)	SS/HS/BD	Hard Segment (HS)	percent HS	Modulus (MPa)	UTS (MPa)	Elongation (percent)
h-HTPBD	Tudos	1552	1/1/0	MDI	14	40.8	3.2	230
h-HTPBD	Tudos	5260	1/5/4	MDI	18	5.8	7.9	431
h-HTPBD	Tudos	1870	1/3/2	MDI	27	50.3	6	57
h-HTPBD	Tudos	1870	1/6/5	MDI	39	279.3	24.6	105
h-HTPBD	Tudos	1245	1/4/3	MDI	40	486.2	32.8	150
h-HTPBD	JSR	1970	1/3/2	MDI	26	12.5	8.9	227
h-HTPBD	JSR	1970	1/6/5	MDI	38	103.5	11.4	85
HTPE	NS	1000	1/1/0	MDI	20	1.6	4.7	43.5
HTPE	NS	2000	1/2/1	MDI	19	3.8	8.9	561
HTPE	NS	3000	1/3/2	MDI	19	3.2	8.4	400
HTPE	NS	2000	1/3/2	MDI	26	11.5	16	370
HTPE	NS	2000	1/6/5	MDI	38	42.1	26.4	270
HTPE	NS	1000	1/3/2	MDI	39	46.8	20.8	285
HTPE	NS	2000	1/3/2	H <sub>12</sub> MDI	27	5.6	11.9	490
HTPE	NS	1000	1/3/2	H <sub>12</sub> MDI	40	74.7	20.9	340

Table 10. Barrier Properties: Part A. Solvent Uptake as a Function of Hard Segment Content

Soft Segment (SS)	SS Source	SS $M_n$ (g/mole)	SS/HS/BD	Hard Segment (HS)	percent HS	CH <sub>3</sub> CN (percent)	DCP (percent)	Toluene (percent)
h-HTPBD	Tudos	5260	1/5/4	MDI	18	3.11	87.9	210
h-HTPBD	Tudos	1870	1/3/2	MDI	27	4.58	46.7	111.6
h-HTPBD	Tudos	1870	1/6/5	MDI	39	--	23.5	--
h-HTPBD	Tudos	1245	1/4/3	MDI	40	6.41	34.5	35.2
h-HTPBD	JSR	1970	1/3/2	MDI	26	41.03	--	196
h-HTPBD	JSR	1970	1/6/5	MDI	38	--	23.2	--
HTPE	NS	1000	1/1/0	MDI	20	4.47	--	273.2
HTPE	NS	2000	1/2/1	MDI	19	2.71	--	216.2
HTPE	NS	3000	1/3/2	MDI	19	2.91	--	163.7
HTPE	NS	2000	1/3/2	MDI	26	37.1	48.9	--
HTPE	NS	2000	1/6/5	MDI	38	9.52	32.5	50.28
HTPE	NS	1000	1/3/2	MDI	39	4.22	33.3	52.4
HTPE	NS	2000	1/3/2	H12MDI	27	15.8	77.7	511.3
HTPE	NS	1000	1/3/2	H12MDI	40	--	75.5	--

Table 11. Barrier Properties: Part B. Diffusion Coefficients as a Function of Hard Segment Content

Soft Segment (SS)	SS Source	SS $M_n$ (g/mole)	SS/HS/BD	Hard Segment (HS)	percent HS	CH <sub>3</sub> CN (cm <sup>2</sup> /s)	DCP (cm <sup>2</sup> /s)	Toluene (cm <sup>2</sup> /s)
h-HTPBD	Tudos	5260	1/5/4	MDI	18	8.46E-08	--	5.14E-08
h-HTPBD	Tudos	1870	1/3/2	MDI	27	4.41E-08	--	3.63E-08
h-HTPBD	Tudos	1870	1/6/5	MDI	39	--	--	--
h-HTPBD	Tudos	1245	1/4/3	MDI	40	1.49E-08	--	5.11E-08
HTPE	NS	1000	1/1/0	MDI	20	1.49E-08	--	2.01E-07
HTPE	NS	2000	1/2/1	MDI	19	1.32E-08	--	1.41E-07
HTPE	NS	3000	1/3/2	MDI	19	3.73E-08	--	4.94E-07
HTPE	NS	2000	1/3/2	MDI	26	3.13E-09	--	--
HTPE	NS	1000	1/3/2	MDI	39	3.01E-08	2.98E-08	3.20E-07

Table 12. Mechanical Properties as a Function of Soft Segment Type

Soft Segment (SS)	SS M <sub>n</sub> (g/mole)	SS/HS/BD	Hard Segment (HS)	percent HS	SS Source	Modulus (MPa)	UTS (MPa)	Elongation (percent)
h-HTPBD	1870	1/3/2	MDI	27	Tudos	50.3	6.0	57
HTPE	2136	1/3/2	MDI	24	Tudos	22.6	20.7	430
h-HTPBD	1970	1/3/2	MDI	26	JSR	12.5	8.9	227
HTPE	2000	1/3/2	MDI	26	NS	11.5	16	370
h-HTPBD	1870	1/6/5	MDI	39	Tudos	279.3	24.6	105
h-HTPBD	1970	1/6/5	MDI	38	JSR	103.5	11.4	85
HTPE	2000	1/6/5	MDI	38	NS	42.1	26.4	270
HTPE	2136	1/3/2	H <sub>12</sub> MDI	25	Tudos	11.2	18.1	483
HTPE	2000	1/3/2	H <sub>12</sub> MDI	27	NS	5.6	11.9	490

Table 13. Barrier Properties: Part A. Solvent Uptake as a Function of Soft Segment Type

Soft Segment (SS)	SS $M_n$ (g/mole)	SS/HS/BD	Hard Segment (HS)	percent HS	SS Source	CH <sub>3</sub> CN (percent)	DCP (percent)	Toluene (percent)
h-HTPBD	1870	1/3/2	MDI	27	Tudos	4.58	46.7	111.6
HTPE	2136	1/3/2	MDI	24	Tudos	2.45	35.8	89.7
h-HTPBD	1970	1/3/2	MDI	26	JSR	41.03	--	196
HTPE	2000	1/3/2	MDI	26	NS	37.1	48.9	--
h-HTPBD	1870	1/6/5	MDI	39	Tudos	--	23.5	--
h-HTPBD	1970	1/6/5	MDI	38	JSR	--	23.2	--
HTPE	2000	1/6/5	MDI	38	NS	9.52	32.5	50.28
HTPE	2136	1/3/2	H <sub>12</sub> MDI	25	Tudos	3.3	47.7	290.4
HTPE	2000	1/3/2	H <sub>12</sub> MDI	27	NS	15.8	77.7	511.3



Table 14. Barrier Properties: Part B. Diffusion Coefficients as a Function of Soft Segment Type

Soft Segment (SS)	SS $M_n$ (g/mole)	SS/HS/BD	Hard Segment (HS)	percent HS	SS Source	CH <sub>3</sub> CN (cm <sup>2</sup> /s)	DCP (cm <sup>2</sup> /s)	Toluene (cm <sup>2</sup> /s)
h-HTPBD	1870	1/3/2	MDI	27	Tudos	4.41E-08	--	3.63E-08
HTPE	2136	1/3/2	MDI	24	Tudos	5.30E-08	--	3.00E-07
h-HTPBD	1970	1/3/2	MDI	26	JSR	--	--	--
HTPE	2000	1/3/2	MDI	26	NS	3.13E-09	--	--
HTPE	2136	1/3/2	H <sub>12</sub> MDI	25	Tudos	1.80E-08	6.13E-08	4.10E-07
HTPE	2000	1/3/2	H <sub>12</sub> MDI	27	NS	2.98E-09	--	2.53E-07

acrylonitrile sorption was particularly striking in comparison to the performance of the Nippon Soda and Japan Synthetic Rubber materials. While diffusion coefficients measured for both the Tudos materials and the Nippon Soda materials were very low overall, the Nippon Soda materials displayed the lowest diffusion coefficients, on the order of  $10^{-9}$  cm<sup>2</sup>/s.

Since the soft segment precursors all have similar polydispersities and functionalities, the differences are most likely attributable to the differences in branch content between the different precursors and the effects of using materials that were hydrogenated before versus after urethane polymerization. The branching content is highest in the Nippon Soda precursors (>80% vinyl), intermediate for the Japan Synthetic Rubber precursors (45% to 55% vinyl), and lowest for the Tudos materials (~15% vinyl). The packing in the Tudos and Nippon Soda materials should be correspondingly better than in the Japan Synthetic Rubber materials because of the more uniform nature of the soft segment structure. This may account partially for the inferior mechanical performance of the Japan Synthetic Rubber urethanes. The low 1,2 branch content in the Tudos materials should lend this system the lowest free volume and best order in the soft segment regions, which may be the origin of the superior solvent resistance observed.

Clearly, the sequence of soft segment hydrogenation versus urethane polymerization has an effect on properties as well. A comparison of the two polymers prepared from nearly identical Tudos precursors underscores the importance of this variable. The Tudos-HTPE-2136-24%HS urethane has both better mechanical properties and barrier properties relative to the Tudos-hHTPBD-1870-27%HS urethane, despite their similarity in formulation. Pre-hydrogenation of the precursors may stabilize them to reduce degradation during storage. Instability during storage may also account for the inferior performance of the urethanes prepared from Japan Synthetic Rubber precursors.

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## 4. Summary

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A series of segmented polyurethane block copolymers based on saturated olefinic soft segments has been prepared. Three types of soft segment precursors were studied, including one novel precursor prepared by isodisperse, telechelic polymerization. These precursors are all based on polybutadiene chemistry but have very different 1,2 to 1,4 addition ratios. The 1,2 contents in the three materials are nominally 15%, 45%, and 80% for precursors prepared by the Tudos group at the Hungarian Academy of Sciences, Japan Synthetic Rubber, and Nippon Soda, respectively. The mechanical and barrier properties of these materials were evaluated.

Overall, the urethane elastomers performed very well. Mechanical properties were found to be superior to those reported in the literature for similar materials, and the urethanes exhibited considerable resistance to swelling and dissolution in common solvents. Diffusion coefficients for the polar and chlorinated solvents studied were found to be extremely low (in the range of  $10^{-8}$  cm<sup>2</sup>/s). The materials based on the Tudos precursors generally outperformed the polymers prepared with the commercial products, although the materials prepared from the Nippon Soda precursors also performed very well.

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